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(54) NITROGEN OXIDES ADSORPTION MATERIAL

(57) Abstract:

PROBLEM TO BE SOLVED: To improve the NO_x adsorptivity at a low temperature zone.

SOLUTION: A adsorption material is constituted with a basic carrier, the platinum deposited by using a platinum colloidal liquid chemical and the palladium deposited by using a palladium salt liquid chemical. Since the platinum exists as relatively large particles

having 1-5 nm particle size, the specific surface area of the platinum is small and hardly oxidized and a metallic state is easy to be kept. Since the platinum is not covered by the palladium, an exposed surface of metallic platinum is enlarged and the NO_x oxidizing activity of the platinum is high. Since formed NO_x is adsorbed to both basic carrier and the palladium, the NO_x adsorptivity is improved.

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CLAIMS

[Claim(s)]

[Claim 1] Nitrogen-oxides adsorption material characterized by consisting of basic support, and the platinum and palladium which were supported by this basic support using the Pt-Pd compound colloid drug solution.

[Claim 2] Nitrogen-oxides adsorption material characterized by consisting of basic support, platinum supported by this basic support using the platinum colloid drug solution, and palladium supported by this basic support using palladium salt glaze liquid.

[Claim 3] Said basic support is nitrogen-oxides adsorption material according to claim 1 or 2 characterized by being ZrO₂.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the nitrogen-oxides adsorption material which adsorbs nitrogen oxides efficiently.

[0002]

[Description of the Prior Art] The three way component catalyst is widely used as a catalyst for emission gas purification which purifies HC, CO, and nitrogen oxides (NOx) which are contained in the exhaust gas from an automobile. This three way component catalyst comes to support noble metals, such as platinum (Pt), a rhodium (Rh), and palladium (Pd), to porosity oxide support, such as an alumina (aluminum 2O3), a silica (SiO2), a zirconia (ZrO2), and a titania (TiO2). This three way component catalyst is NOx while oxidizing and purifying HC and CO in exhaust gas. It returns, and it can purify and can purify most effectively in the exhaust gas of the SUTOIKI ambient atmosphere which burned in the SUTOIKI ambient atmosphere near the theoretical air fuel ratio.

[0003] Moreover, the lean burn engine which burns in a hyperoxia ambient atmosphere for the purpose of reduction of a carbon dioxide (CO2) is used in recent years. This lean burn engine is burned on the Lean conditions of hyperoxia, makes exhaust gas reducing atmosphere by considering as SUTOIKI - rich conditions temporarily, and is always NOx. It is driving by the system which carries out reduction purification. And as the optimal catalyst for this system, it is NOx at lean atmosphere. NOx by which carried out occlusion and occlusion was carried out in the SUTOIKI - rich ambient atmosphere NOx to emit The catalyst for emission gas purification of the NOx occlusion reduction type using an occlusion element is developed.

[0004] This NOx At the Lean side, it is NOx by controlling an air-fuel ratio to consist pulse-like of a Lean side a SUTOIKI - rich side, if an occlusion reduction type catalyst is used. NOx It is NOx even if it is exhaust gas from a lean burn engine, since occlusion is carried out to an occlusion element, it is emitted by SUTOIKI or the rich side, it reacts with reducibility components, such as HC and CO, and it is purified. It can purify efficiently. Thus, controlling an air-fuel ratio to become pulse-like a SUTOIKI - rich side is expressed as "the rich spike."

[0005] And NOx which becomes JP,7-163871,A from CeO2 etc. Adsorption material is indicated and it is NOx. It is NOx by combining with a reduction catalyst etc. Raising purification activity is indicated.

[0006] However, HC and NOx in a low-temperature region since purification becomes difficult in the conventional three way component catalyst in the low-temperature region below catalytic activity temperature of noble metals, such as the time of engine starting, There is a problem that decontamination capacity is low.

[0007] Moreover, NOx Exhaust gas temperature is at an occlusion reduction type catalyst. NOx in a less than 300-degree C low-temperature region It is NOx, so that occlusion ability is inadequate and it becomes a low-temperature region. There is fault that occlusion ability falls. Therefore, when the exhaust gas at the time starting and between the colds etc. is in a low-temperature region, it compares with a pyrosphere, and it is NOx. There was a problem that decontamination capacity fell.

[0008] And in JP,7-163871,A, it is NOx. It is NOx by adsorption material. It is NOx in the low-temperature region of less than 300 degrees C although it is indicated that decontamination capacity improves. There is no publication about purification.

[0009]

[Problem(s) to be Solved by the Invention] this invention persons are NOx as a result of inquiring wholeheartedly about the purification behavior of a catalyst. By contacting the removed exhaust gas for

the catalyst for emission gas purification, HC and CO discovered being efficiently purified from a low-temperature region. And by arranging nitrogen-oxides adsorption material to the upstream of the catalyst for emission gas purification, HC and CO could be purified from the low-temperature region, and it became clear that a purification temperature window spreads. The cause which becomes such is NOx although it is not clear. That the reactivity of HC, and CO and O₂ improved in not existing, and NOx It is possible to be hard to produce poisoning on the front face of noble metals to depend etc.

[0010] That is, nitrogen-oxides adsorption material is NOx. It is easy to adsorb and NOx also in a low-temperature region. It adsorbs. Therefore, nitrogen-oxides adsorption material is arranged to the upstream of emission, and it is NOx to the downstream. If the occlusion reduction type catalyst is arranged, it will set in a low-temperature region, and it is NOx. The hardly included exhaust gas is NOx. Since an occlusion reduction type catalyst is supplied, it is NOx. In the exhaust gas discharged from an occlusion reduction type catalyst, it is NOx. It is hardly contained. And NOx currently adsorbed when exhaust gas temperature rose It is desorbed from nitrogen-oxides adsorption material, and is NOx. An occlusion reduction type catalyst is supplied and it is NOx. Reduction purification is carried out with an occlusion reduction type catalyst.

[0011] As this nitrogen-oxides adsorption material, transition-metals oxides, such as the oxide of alkali metal, the oxide of alkaline earth metal, an oxide of rare earth elements, Co 3O₄, NiO₂ and MnO₂, Fe₂O₃, and ZrO₂, a zeolite, etc. are illustrated. it is independent about these -- it is -- two or more kinds can be combined and it can consider as nitrogen-oxides adsorption material. moreover -- aluminum² -- what supported the metallic element chosen as porosity oxide support, such as O₃, SiO₂, SiO₂-aluminum 2O₃, ZrO₂ and TiO₂, and a zeolite, from alkali metal, alkaline earth metal, and rare earth elements can be used.

[0012] Moreover, it compares with acid support, such as TiO₂, and basic support, such as ZrO₂, is NOx. It is easy to adsorb. Therefore, especially the thing that added alkali metal and alkaline earth metal to ZrO₂ is NOx which was excellent as compared with other nitrogen-oxides adsorption material.

Adsorption capacity is shown. and ZrO₂ which added alkali metal and alkaline earth metal -- noble metals, such as Pt, Rh, and Pd, -- or -- if transition-metals oxides, such as Co 3O₄, NiO₂ and MnO₂, and Fe 2O₃, are supported -- NOx Adsorption capacity improves further. This is Pt. Oxidation activity is discovered with Co 3O₄, NiO₂ and MnO₂, Fe 2O₃, etc., and NO in exhaust gas is NO₂. It is NOx by oxidizing. It thinks for the amount of adsorption to increase.

[0013] However, for low-temperature adsorbent ones, the nitrogen-oxides adsorption material which was described above according to the further research of this invention persons is NOx although it is high. A rate of adsorption is NOx late. The amount of adsorption also became clear [few things].

[0014] It is made in view of such a situation, and this invention is NOx. NOx [in / it is raising adsorption capacity and / a low-temperature region] It aims at raising adsorption capacity further.

[0015]

[Means for Solving the Problem] The description of the nitrogen-oxides adsorption material of this invention which solves the above-mentioned technical problem is to consist of basic support, and Pt and Pd which were supported by basic support using the Pt-Pd compound colloid drug solution.

[0016] The description of the nitrogen-oxides adsorption material of another this invention which solves the above-mentioned technical problem is to consist of basic support, Pt supported by basic support using the platinum colloid drug solution, and Pd supported by basic support using Pd salt glaze liquid.

[0017] As for basic support, in two kinds of above-mentioned nitrogen-oxides adsorption material, it is desirable that it is ZrO₂.

[0018]

[Embodiment of the Invention] NO in exhaust gas oxidizes, although the extent basicity support which is also itself is adsorbed, and it is NOx. It is thought by becoming that it becomes that it is easy to adsorb by basic support. Then, NOx of nitrogen-oxides adsorption material A rate of adsorption is raised and it is NOx. In order to increase the amount of adsorption, it is effective to promote oxidation reaction of NO.

[0019] Oxidation activity of Pt is very high and it is the the best for promotion of oxidation reaction of NO. However, when Pt serves as platinum oxide or is covered by other elements, it has the fault that oxidation activity will fall. For example, since Pt supported using the common platinum complex salt water solution etc. is supported as the shape of a detailed atom, it oxidizes, and it tends to be set to PtO₂ etc.

[0020] So, Pt is supported with this invention using a Pt-Pd compound colloid drug solution or Pt colloid drug solution. Thus, the particle size for which the atoms of 10 - a-1000 number gathered serves as a comparatively big particle which is 1-5nm, and supported Pt exists. It is thought that this is easy to

maintain a metal condition, and since a support condition becomes metalmore nearly -like, the oxidation activity of NO improves further by activating the electronic transfer between NO and Pt more.

[0021] Moreover, in Pd, it is NOx. It became clear that there is a property of adsorbing. Therefore, it is NOx by supporting Pd to basic support. Adsorption sites increase in number and it is NOx. The amount of adsorption increases. Then, the nitrogen-oxides adsorption material of this invention consists of basic support, and Pt and Pd which were supported by basic support. since Pt is excellent in oxidation ability -- NO in exhaust gas -- oxidizing -- NO2 etc. -- NOx ** -- it carries out. This NOx While sticking to basic support, in order to stick also to Pd, the nitrogen-oxides adsorption material of this invention is high NOx. It has adsorption capacity.

[0022] The oxidation of NO by Pt, and NOx by Pd In order to adsorb still more efficiently, it is desirable to carry out contiguity support of Pt and the Pd. So, Pt and Pd are supported with one nitrogen-oxides adsorption material of this invention using the Pt-Pd compound colloid drug solution. By supporting with Pt-Pd compound colloid using a Pt-Pd compound colloid drug solution, since Pd particle is a colloidal particle in the condition that more than one adhered, around the particle of Pt, contiguity support of Pt and the Pd can be carried out, and, thereby, it is NOx. Adsorption capacity improves further.

[0023] However, since Pt is in the condition of having been covered with Pd when it supports using a Pt-Pd compound colloid drug solution, the oxidation activity of NO by Pt falls, and it is NOx. There is concern to which adsorption capacity falls. So, while supporting Pt using Pt colloid drug solution, Pd is supported with another nitrogen-oxides adsorption material of this invention using Pd salt glaze liquid. Thereby, since Pt is supported with the comparatively big particle as colloid and Pd is supported with a detailed atom-like condition by homogeneity, there is no fault which Pd condenses and covers around Pt. Therefore, it is NOx of Pd, being able to enlarge metal-like expressional area of Pt and maintaining the oxidation activity of Pt highly. Adsorption activity can be made to discover.

[0024] As basic support, ZrO₂, aluminum 2O₃, MgAl 2O₄, MgO, etc. are illustrated. Basicity is high especially and it is NOx. NOx to which it excelled in the adsorption property and stuck Especially ZrO₂ that is easy to emit at the time of a rich spike is desirable. Moreover, it is NOx, while thermal stability will improve and endurance will improve, if ZrO₂ containing at least one element chosen from La, K, and calcium is used. A rate of adsorption and NOx The amount of adsorption improves further.

[0025] This element dissolves in ZrO₂ grid, although it is not clear, it is compound-ized and reforming of the ZrO₂ </SUB> front face is carried out by it, and the cause with effective addition of such an element is newly NOx. It is thought that it will be because an adsorption site is generated.

[0026] In addition, as for the content of at least one element chosen from La, K, and calcium, it is desirable to consider as the 1-10-mol range of %. If it is difficult to maintain thermal stability if there are few contents than this range and it increases more than this range, it is NOx of ZrO₂. The hydroxyl group which is an adsorption site cannot be used effectively, but it is NOx. It is NOx while adsorption capacity falls. Decontamination capacity also falls.

[0027] A noble-metals colloid drug solution can be prepared by mixing and heating a water-soluble noble-metals salt and alcohol, and forming macromolecule protection noble-metals colloid into the water solution of water soluble polymers, such as a polyvinyl pyrrolidone and polyvinyl alcohol. This approach is called the macromolecule protecting method. And the basic support powder described above in the water solution of this macromolecule protection noble-metals colloid can be distributed, and noble metals can be supported with drying and calcinating it as a comparatively big particle. Moreover, you may support using the approach of using an electrostatic effect, the method of using adsorption to the support of a macromolecule chain, etc.

[0028] As a particle size of Pt currently supported using the Pt-Pd compound colloid drug solution or Pt colloid drug solution, it is desirable to consider as the range of 1-5nm. Theoretically, 1-5nm, then a configuration atomic number are set to 10-3000 in particle size. Since it will become close to an atomic condition and Pd will become is easy to be covered if the particle size of Pt is smaller than 1nm, it is NOx by the fall of NO oxidation activity. Adsorption capacity falls. Moreover, since surface area will fall if particle size becomes larger than 5nm, the active spot decreases, and it is NOx by the fall of NO oxidation activity. Adsorption capacity falls.

[0029] As Pd salt glaze liquid, acid drug solutions, such as a palladium nitrate and a palladium chloride, can be used. In addition, the sequence is not asked, when supporting Pt using Pt colloid drug solution and supporting Pd using Pd salt glaze liquid. Especially the thing for which Pt is supported with it after supporting Pd first especially is desirable. If it does in this way, since it is certainly avoidable that Pt is covered with Pd, it is especially high NOx. Adsorption capacity is discovered.

[0030] The amount of support of Pt is basic support. The range of per [1-5g] 120g is desirable. If there

are few amounts of support than this, it is NOx by the fall of NO oxidation activity. Adsorption capacity becomes low, and it becomes a cost rise while effectiveness is saturated, even if it supports mostly from this. Moreover, the amount of support of Pd is basic support. Per 120g The range of 0.5-2.5g is desirable. If there are few amounts of support than this, it is NOx by the fall of NO adsorption activity. Adsorption capacity becomes low, and it becomes a cost rise while effectiveness is saturated, even if it supports mostly from this.

[0031] And the nitrogen-oxides adsorption material of this invention can be used for the following emission-gas-purification approaches. That is, the nitrogen-oxides adsorption material of this invention is first arranged in the exhaust gas of the lean atmosphere of hyperoxia, and it is NOx in exhaust gas. It adsorbs. NO in exhaust gas oxidizes efficiently by the catalysis of Pt, and is NOx. It becomes and basic support and Pd are adsorbed efficiently. Therefore, it also sets in a low-temperature region and is NOx. It often adsorbs and the amount of adsorption also has many rate of adsorptions greatly. Although there is no limit especially as this lean atmosphere, the exhaust gas ambient atmosphere which burned considering the air-fuel ratio (A/F) as 15-50 is suitable.

[0032] Then, NOx by which nitrogen-oxides adsorption material was adsorbed when the oxygen density in exhaust gas was reduced temporarily and it was a SUTOIKI - rich ambient atmosphere NOx emitted and emitted It reacts with CO in exhaust gas, HC, etc. by the metal-like catalysis of Pt and Pd currently supported, and reduction purification is carried out. Although this SUTOIKI - especially a rich ambient atmosphere are not restricted, either, the exhaust gas ambient atmosphere which burned considering the air-fuel ratio (A/F) as ten to about 14 is suitable. Moreover, the time amount or the frequency of a rich spike where an oxygen density is reduced temporarily can be variously set up according to the purpose.

[0033] As described above, at least the nitrogen-oxides adsorption material of this invention is NOx. Adsorbing and returning is possible. However, NOx In order to carry out reduction purification still more efficiently, they are a three way component catalyst or NOx to the emission way of the downstream of the nitrogen-oxides adsorption material of this invention. It is desirable to arrange an occlusion reduction type catalyst. NOx which it is emitted by this from nitrogen-oxides adsorption material, and was not able to be returned in nitrogen-oxides adsorption material NOx [in / reduction purification can be carried out with the catalyst of the downstream and / a SUTOIKI - rich ambient atmosphere] A discharge can be reduced further. Moreover, it is NOx to the catalyst of the downstream. NOx [in / like the above / a SUTOIKI - rich ambient atmosphere] if an occlusion reduction type catalyst is used While being able to reduce a discharge further, it is NOx in exhaust gas. NOx to which it was not able to stick by nitrogen-oxides adsorption material mostly unusually NOx NOx in the lean atmosphere of hyperoxia since occlusion can be carried out to an occlusion reduction type catalyst A discharge can also be reduced further.

[0034]

[Example] Hereafter, an example and the example of a comparison explain this invention concretely.

[0035] (Example 1) Water To 200g The water solution which mixed [PtCl4 (5H2O)] 2.8418g with 2.1893g for PdCl3 (3H2O), and water The water solution which mixed polyvinyl-pyrrolidone 5.74g of the 200g number average molecular weight 25,000 was prepared, respectively, it agitated after mixing both water solutions, and the uniform water solution was prepared. In this water solution 200g ethanol was added, it returned at 90 degrees C for 4 hours, and the Pt-Pd compound colloid (Pt:50 % of the weight, Pd:50 % of the weight) drug solution was obtained.

[0036] ZrO2 powder of the specified quantity is thrown in in this Pt-Pd compound colloid drug solution -- at 200 degree C, it agitated for about 2 hours and evaporation to dryness was carried out. This It is after 2-hour desiccation at 120 degrees C. It calcinated at 500 degrees C for 2 hours, and nitrogen-oxides adsorption material powder was obtained. With this nitrogen-oxides adsorption material powder, it is ZrO2. 1g and 1g of Pd are supported for Pt to 120g. This powder CIP shaping is carried out on the conditions for 65MPax 2 minutes, it is ground, and it is magnitude. It considered as the pellet type of 0.5 to 0.8 mm.

[0037] (Example 2) Water 200g The water solution which mixed PtCl4 (5H2O) 4.3786g, and water The water solution which mixed polyvinyl-pyrrolidone 5.74g of number average molecular weight 25,000 to 200g was prepared, respectively, it agitated after mixing both water solutions, and the uniform water solution was prepared. In this water solution 100g ethanol was added, it flowed back at 90 degrees C for 4 hours, and Pt colloid drug solution was obtained.

[0038] On the other hand, ZrO2 powder of the specified quantity is thrown in in the specified quantity of the palladium nitrate water solution of predetermined concentration, at 200 degrees C, it agitated for about 2 hours and evaporation to dryness was carried out. This It is after 2-hour desiccation at 120 degrees C. It calcinated at 500 degrees C for 2 hours, and Pd/ZrO2 powder was obtained.

[0039] next, this Pd/ZrO₂ powder is thrown in in the above-mentioned Pt colloid drug solution -- at 200 degree C, it agitated for about 2 hours and evaporation to dryness was carried out. This It is after 2-hour desiccation at 120 degrees C. It calcinated at 500 degrees C for 2 hours, and Pt was supported further. With this nitrogen-oxides adsorption material powder, it is ZrO₂. 1g of Pt(s) is supported to 120g, and 1g of Pd is supported. This powder CIP shaping is carried out on the conditions for 65MPax 2 minutes, it is ground, and it is magnitude. It considered as the pellet type of 0.5 to 0.8 mm.

[0040] (Example 3) Water 200g The water solution which mixed PtCl₄ (5H₂O)4.3786g, and water The water solution which mixed polyvinyl-pyrrolidone 5.74g of number average molecular weight 25,000 to 200g was prepared, respectively, it agitated after mixing both water solutions, and the uniform water solution was prepared. In this water solution 100g ethanol was added, it flowed back at 90 degrees C for 4 hours, and Pt colloid drug solution was obtained.

[0041] Pt colloid drug solution is thrown in after [after throwing in ZrO₂ powder in a palladium nitrate water solution] about 5 minutes -- at 200 degree C, it agitated for about 2 hours and evaporation to dryness was carried out. This It calcinated at 500 degrees C after 2-hour desiccation by 120 degrees C for 2 hours, and nitrogen-oxides adsorption material powder was obtained. With this nitrogen-oxides adsorption material powder, it is ZrO₂. 1g and 1g of Pd are supported for Pt to 120g. CIP shaping of this powder is carried out on the conditions for 65MPa(s)x 2 minutes, it is ground, and it is magnitude. It considered as the pellet type of 0.5 to 0.8 mm.

[0042] (Example 1 of a comparison) Water 200g The water solution which mixed PtCl₄ (5H₂O)4.3786g, and water The water solution which mixed polyvinyl-pyrrolidone 5.74g of number average molecular weight 25,000 to 200g was prepared, respectively, it agitated after mixing both water solutions, and the uniform water solution was prepared. In this water solution 100g ethanol was added, it flowed back at 90 degrees C for 4 hours, and Pt colloid drug solution was obtained.

[0043] ZrO₂ powder is thrown in in this Pt colloid drug solution -- at 200 degree C, it agitated for about 2 hours and evaporation to dryness was carried out. This It is after 2-hour desiccation at 120 degrees C. It calcinated at 500 degrees C for 2 hours, and nitrogen-oxides adsorption material powder was obtained. With this nitrogen-oxides adsorption material powder, it is ZrO₂. 2g of Pt(s) is supported to 120g. This powder CIP shaping is carried out on the conditions for 65MPax 2 minutes, it is ground, and it is magnitude. It considered as the pellet type of 0.5 to 0.8 mm.

[0044] (Example 2 of a comparison) Water To 200g The water solution which mixed 2.1893g and RhCl₃ (3H₂O) 2.5597g for PtCl₄ (5H₂O), and water The water solution which mixed polyvinyl-pyrrolidone 5.74g of the 200g number average molecular weight 25,000 was prepared, respectively, it agitated after mixing both water solutions, and the uniform water solution was prepared. In this water solution 100g ethanol was added, it returned at 90 degrees C for 4 hours, and the Pt-Rh compound colloid (Pt:50 % of the weight, Rh:50 % of the weight) drug solution was obtained.

[0045] ZrO₂ powder is thrown in in this Pt-Rh compound colloid drug solution -- at 200 degree C, it agitated for about 2 hours and evaporation to dryness was carried out. This It is after 2-hour desiccation at 110 degrees C. It calcinated at 500 degrees C for 2 hours, and nitrogen-oxides adsorption material powder was obtained. With this nitrogen-oxides adsorption material powder, it is ZrO₂. 1g and 1g of Rh(s) are supported for Pt to 120g. This powder CIP shaping is carried out on the conditions for 65MPax 2 minutes, it is ground, and it is magnitude. It considered as the pellet type of 0.5 to 0.8 mm.

[0046] <A trial and evaluation> Each nitrogen-oxides adsorption material has been arranged to evaluation equipment, and NO amount of adsorption was measured on the conditions shown in drawing 1, respectively. first -- N₂ gas ambient atmosphere -- a part for programming-rate/of 17.5 degrees C -- from a room temperature it heats to 450 degrees C -- it holds for 10 minutes at 450 degree C. After that It cools to 100 degrees C and the model gas shown in Table 1 is passed. For [NO] 30 minutes is made to adsorb at 100 degrees C. The flow rate of model gas is a part for 7L/. a part for after that programming-rate/of 17.5 degrees C it heats to 450 degrees C -- it holds for 10 minutes at 450 degree C. And NO_x in appearance gas Concentration was measured continuously and NO amount of adsorption was calculated. Each result is shown in drawing 2.

[0047] If NO carries out saturation adsorption at nitrogen-oxides adsorption material, NO will be bypassed after that, without adsorbing, after being set to NO_x (x> 1) on Pt. Therefore, it can come out with the entering gas at that time (NO), and the difference of gas (NO+NO_x) can be made into the index of NO oxidation activity.

[0048]

[Table 1]

ガス種	NO (ppm)	O ₂ (%)	CO (%)	H ₂ O (%)	N ₂
濃度	800	10	6.7	3	残部

[0049] The nitrogen-oxides adsorption material of each example has much NO amount of adsorption compared with the example 1 of a comparison, and it is clearer than drawing 2 that its it is the effectiveness resulting from having supported Pd further in addition to Pt while this supports Pt as a compound colloid drug solution.

[0050] Moreover, when examples are compared, it turns out that to support using a palladium nitrate drug solution is more desirable rather than the direction of an example 2 has much NO amount of adsorption and supports Pd using a Pt-Pd compound colloid drug solution from an example 1.

[0051] Moreover, in the example 3, although there is less NO amount of adsorption than the example 2 acquired using the same raw material, since Pt was covered with Pd since Pt and Pd were supported with the example 3 to coincidence, and NO oxidation activity fell, this is considered. Therefore, it is clear that it is optimal to support Pd using a palladium nitrate drug solution first, and to support Pt using Pt colloid drug solution after that.

[0052] Furthermore, by neither of nitrogen-oxides adsorption material of the Pt-Rh system of the example 2 of a comparison, in spite of supporting Pt and Rh using a compound colloid drug solution, there is less NO amount of adsorption than the example 1 of a comparison, and the activity like the Pt-Pd system of an example 1 is acquired at all. For future and Rh, it turns out that it is completely ineffective and Pd has discovered unique effectiveness, and Pd is NOx. It is suggested that it is an adsorption site.

[0053]

[Effect of the Invention] Namely, NOx [according to the nitrogen-oxides adsorption material of this invention] in a low-temperature region There is much amount of adsorption and it is NOx. It excels in adsorption capacity. Therefore, NOx in a low-temperature region if the nitrogen-oxides adsorption material of this invention is used for the exhaust gas system of an automobile Discharge can be controlled further and it is NOx. The rate of purification also improves.

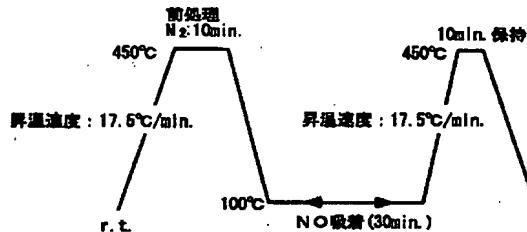
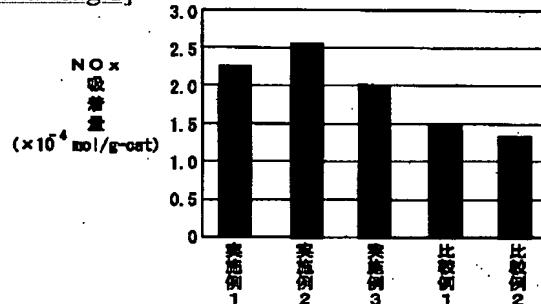
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DRAWINGS

[Drawing 1]**[Drawing 2]**

[Translation done.]

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(54) 【発明の名称】 窒素酸化物吸着材

(57) 【要約】

【課題】 低温域におけるNO_x 吸着能をさらに向上させる。

【解決手段】 塩基性担体と、Ptコロイド薬液を用いて担持されたPtと、Pd塩薬液を用いて担持されたPdとから構成した。Ptは粒径が1～5nmの比較的大きな粒子となって存在しているので、比表面積が小さく酸化されにくいため金属状態を維持しやすい。またPtがPdによって覆われるのが防止されているため、金属ライクなPtの表出面積が大きくなり、PtのNO_x酸化活性が高い。そして生成したNO_x は塩基性担体とPdの両方に吸着するので、NO_x 吸着能が向上する。

【特許請求の範囲】

【請求項1】 塩基性担体と、Pt-Pd複合コロイド薬液を用いて該塩基性担体に担持された白金及びパラジウムによりなることを特徴とする窒素酸化物吸着材。

【請求項2】 塩基性担体と、白金コロイド薬液を用いて該塩基性担体に担持された白金と、パラジウム塩薬液を用いて該塩基性担体に担持されたパラジウムによりなることを特徴とする窒素酸化物吸着材。

【請求項3】 前記塩基性担体はZrO₂であることを特徴とする請求項1又は請求項2に記載の窒素酸化物吸着材。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は窒素酸化物を効率よく吸着する窒素酸化物吸着材に関する。

【0002】

【従来の技術】 自動車からの排ガス中に含まれるHC、CO及び窒素酸化物(NO_x)を浄化する排ガス浄化用触媒として、三元触媒が広く用いられている。この三元触媒は、アルミナ(Al₂O₃)、シリカ(SiO₂)、ジルコニア(ZrO₂)、チタニア(TiO₂)などの多孔質酸化物担体に、白金(Pt)、ロジウム(Rh)、パラジウム(Pd)などの貴金属を担持してなるものである。この三元触媒は、排ガス中のHC及びCOを酸化して浄化するとともに、NO_xを還元して浄化するものであり、理論空燃比近傍のトイキ雾囲気で燃焼されたトイキ雾囲気の排ガスにおいて最も効果的に浄化することができる。

【0003】 また近年、二酸化炭素(CO₂)の低減を目的として酸素過剰雾囲気で燃焼するリーンバーンエンジンが用いられている。このリーンバーンエンジンは、當時は酸素過剰のリーン条件で燃焼させ、一時的にトイキ～リッチ条件とすることにより排ガスを還元雾囲気としてNO_xを還元浄化するシステムによって駆動されている。そしてこのシステムに最適な触媒として、リーン雾囲気でNO_xを吸着し、トイキ～リッチ雾囲気で吸着されたNO_xを放出するNO_x吸着元素を用いたNO_x吸着還元型の排ガス浄化用触媒が開発されている。

【0004】 このNO_x吸着還元型触媒を用いれば、空燃比をリーン側からパルス状にトイキ～リッチ側となるように制御することにより、リーン側ではNO_xがNO_x吸着元素に吸着され、それがトイキ又はリッチ側で放出されてHCやCOなどの還元性成分と反応して浄化されるため、リーンバーンエンジンからの排ガスであってもNO_xを効率良く浄化することができる。このようにパルス状にトイキ～リッチ側となるように空燃比を制御することは、「リッチスパイク」と表現されている。

【0005】 そして特開平7-163871号公報には、CeO₂などからなるNO_x吸着材が開示され、NO_x還元触媒などと組み合わせることでNO_x浄化活性を高めることができることが記載されている。

【0006】 ところが従来の三元触媒においては、エンジン始動時など貴金属の触媒活性温度以下の低温域では浄化が困難となるために、低温域におけるHCやNO_xの浄化能が低いという問題がある。

【0007】 またNO_x吸着還元型触媒では、排ガス温度が特に300℃未満の低温域におけるNO_x吸着能が不充分であり、低温域になるほどNO_x吸着能が低下するという不具合がある。そのため始動時や冷間時などの排ガスが低温域にある場合には、高温域に比べてNO_x浄化能が低下するという問題があった。

【0008】 そして特開平7-163871号公報には、NO_x吸着材によってNO_x浄化能が向上することは記載されているものの、300℃未満の低温域におけるNO_xの浄化に関する記載はない。

【0009】

【発明が解決しようとする課題】 本発明者らは、触媒の浄化挙動について鋭意研究した結果、NO_xが除去された排ガスを排ガス浄化用触媒に接触させることにより、HC及びCOが低温域から効率よく浄化されることを発見した。そして排ガス浄化用触媒の上流側に窒素酸化物吸着材を配置することで、低温域からHC及びCOを浄化することができ、浄化温度ウィンドウが拡がることが明らかとなった。このようになる原因は明らかではないが、NO_xが存在しないことでHC及びCOとO₂との反応性が向上したこと、NO_xによる貴金属表面の被毒が生じにくいことなどが考えられる。

【0010】 つまり窒素酸化物吸着材はNO_xを吸着しやすく、低温域でもNO_xを吸着する。したがって排ガス流の上流側に窒素酸化物吸着材を配置し、その下流側にNO_x吸着還元型触媒を配置しておけば、低温域においてはNO_xをほとんど含まない排ガスがNO_x吸着還元型触媒に供給されるので、NO_x吸着還元型触媒から排出される排ガス中にはNO_xはほとんど含まれない。そして排ガス温度が上昇すると、吸着されていたNO_xが窒素酸化物吸着材から脱離してNO_x吸着還元型触媒に供給され、NO_x吸着還元型触媒で還元浄化される。

【0011】 この窒素酸化物吸着材としては、アルカリ金属の酸化物、アルカリ土類金属の酸化物、希土類元素の酸化物、Co₃O₄、NiO₂、MnO₂、Fe₂O₃、ZrO₂などの遷移金属酸化物、ゼオライトなどが例示される。これらを単独であるいは複数種類組み合わせて窒素酸化物吸着材とすることができます。またAl₂O₃、SiO₂、SiO₂-Al₂O₃、ZrO₂、TiO₂、ゼオライトなどの多孔質酸化物担体にアルカリ金属、アルカリ土類金属及び希土類元素から選ばれる金属元素を担持したものなども用いることができる。

【0012】 またZrO₂などの塩基性担体は、TiO₂などの酸性担体に比べてNO_xを吸着しやすい。したがってZrO₂にアルカリ金属やアルカリ土類金属を添加したものは、他の窒素酸化物吸着材と比較して特に優れたNO_x吸着能を示す。そして、アルカリ金属やアルカリ土類金属を添

加したZrO₂に、Pt, Rh, Pdなどの貴金属、あるいはCo₃O₄, NiO₂, MnO₂, Fe₂O₃などの遷移金属酸化物を担持すると、NO_x吸着能がさらに向上する。これは、PtやCo₃O₄, NiO₂, MnO₂, Fe₂O₃などによって酸化活性が発現し、排ガス中のNOがNO₂に酸化されることによってNO_x吸着量が増加するためと考えられている。

【0013】ところが本発明者らのさらなる研究によれば、上記した窒素酸化物吸着材は、低温吸着性は高いものの、NO_xの吸着速度が遅くNO_xの吸着量も少ないことが明らかとなった。

【0014】本発明はこのような事情に鑑みてなされたものであり、NO_x吸着能を向上させることで、低温域におけるNO_x吸着能をさらに向上させることを目的とする。

【0015】

【課題を解決するための手段】上記課題を解決する本発明の窒素酸化物吸着材の特徴は、塩基性担体と、Pt-Pd複合コロイド薬液を用いて塩基性担体に担持されたPt及びPdとよりなることにある。

【0016】上記課題を解決するもう一つの本発明の窒素酸化物吸着材の特徴は、塩基性担体と、白金コロイド薬液を用いて塩基性担体に担持されたPtと、Pd塩薬液を用いて塩基性担体に担持されたPdとよりなることにある。

【0017】上記した2種類の窒素酸化物吸着材において、塩基性担体はZrO₂であることが望ましい。

【0018】

【発明の実施の形態】排ガス中のNOは、それ自体でもある程度塩基性担体に吸着されるが、酸化されてNO_xとなることによって塩基性担体により吸着されやすくなると考えられる。そこで窒素酸化物吸着材のNO_xの吸着速度を向上させ、かつNO_xの吸着量を増大させるためには、NOの酸化反応を促進することが有効である。

【0019】Ptはきわめて酸化活性が高く、NOの酸化反応の促進に最適である。ところがPtは、酸化白金となったり、他の元素で覆われたりすると酸化活性が低下してしまうという不具合がある。例えば一般的な白金錯塩水溶液などを用いて担持されたPtは、微細な原子状として担持されているため酸化されてPtO₂などになりやすい。

【0020】そこで本発明では、PtをPt-Pd複合コロイド薬液又はPtコロイド薬液を用いて担持している。このようにして担持されたPtは、10～数1000の原子が集まつた粒径が1～5nmの比較的大きな粒子となって存在している。これにより金属状態を維持しやすいと考えられ、担持状態がより金属ライクとなるためNOとPtとの間の電子授受がより活発化されることによってNOの酸化活性がさらに向上する。

【0021】またPdには、NO_xを吸着する特性があることが明らかとなった。したがってPdを塩基性担体に担持することによってNO_xの吸着サイトが増え、NO_x吸着量

が増大する。そこで本発明の窒素酸化物吸着材は、塩基性担体と、塩基性担体に担持されたPt及びPdとから構成されている。Ptは酸化能に優れるため、排ガス中のNOを酸化してNO₂などのNO_xとする。このNO_xが塩基性担体に吸着するとともに、Pdにも吸着するため、本発明の窒素酸化物吸着材は高いNO_x吸着能を有している。

【0022】PtによるNOの酸化とPdによるNO_xの吸着とをさらに効率よく行うためには、PtとPdとを近接担持することが望ましい。そこで本発明の一つの窒素酸化物吸着材では、Pt及びPdはPt-Pd複合コロイド薬液を用いて担持されている。Pt-Pd複合コロイドでは、Ptの粒子の周りにPd粒子が複数個付着した状態のコロイド粒子となつているため、Pt-Pd複合コロイド薬液を用いて担持することによりPtとPdを近接担持することができ、これによりNO_x吸着能がさらに向上する。

【0023】ところがPt-Pd複合コロイド薬液を用いて担持した場合には、PtがPdによって覆われた状態となつているため、PtによるNOの酸化活性が低下しNO_x吸着能が低下する懸念がある。そこで本発明のもう一つの窒素酸化物吸着材では、PtをPtコロイド薬液を用いて担持するとともに、PdをPd塩薬液を用いて担持している。これによりPtはコロイドとして比較的大きな粒子で担持され、Pdは原子状の微細な状態で均一に担持されるので、Ptの周囲にPdが凝集して覆うような不具合がない。したがって金属ライクなPtの表面面積を大きくすることができ、Ptの酸化活性を高く維持したままPdのNO_x吸着活性を発現させることができる。

【0024】塩基性担体としては、ZrO₂, Al₂O₃, MgAl₂O₄, MgOなどが例示される。中でも塩基性が高くNO_xの吸着特性に優れ、かつ吸着したNO_xをリッチスパイク時に放出しやすいZrO₂が特に好ましい。またLa, K及びCaから選ばれる少なくとも一つの元素を含むZrO₂を用いれば、熱安定性が向上し耐久性が向上するとともに、NO_x吸着速度及びNO_x吸着量が一層向上する。

【0025】このような元素の添加が効果的な原因は明らかではないが、この元素がZrO₂格子中に固溶して複合化され、それによってZrO₂表面が改質されて新たにNO_x吸着サイトが生成されるからであろうと考えられる。

【0026】なおLa, K及びCaから選ばれる少なくとも一つの元素の含有量は、1～10モル%の範囲とすることが望ましい。含有量がこの範囲より少ないと熱安定性を保つのが困難であり、この範囲より多くなるとZrO₂のNO_x吸着サイトである水酸基を有効に利用できず、NO_xの吸着能が低下するとともにNO_x浄化能も低下する。

【0027】貴金属コロイド薬液は、ポリビニルピロリドン、ポリビニルアルコールなどの水溶性高分子の水溶液中に水溶性貴金属塩とアルコールを混合して加熱し、高分子保護貴金属コロイドを形成することで調製することができる。この方法は高分子保護法と称されている。

50 そして、この高分子保護貴金属コロイドの水溶液中に上

記した塩基性担体粉末を分散させ、それを乾燥・焼成することで貴金属を比較的大きな粒子として担持することができる。また、静電効果を利用する方法、高分子鎖の担体への吸着を利用する方法などを用いて担持してもよい。

【0028】Pt-Pd複合コロイド薬液又はPtコロイド薬液を用いて担持されているPtの粒径としては、1～5nmの範囲とすることが好ましい。理論的には、粒径を1～5nmとすれば構成原子数は10～3000となる。Ptの粒径が1nmより小さいと原子状態に近くなり、Pdに覆われやすくなるためNO_x酸化活性の低下によりNO_xの吸着能が低下する。また粒径が5nmより大きくなると表面積が低下するため活性点が少なくなり、NO_x酸化活性の低下によりNO_xの吸着能が低下する。

【0029】Pd塩薬液としては硝酸パラジウム、塩化パラジウムなどの酸性の薬液を用いることができる。なおPtをPtコロイド薬液を用いて担持し、PdをPd塩薬液を用いて担持する場合、その順序は問わない。なかでも、先ずPdを担持した後にPtを担持することが特に望ましい。このようにすれば、PtがPdによって覆われるのを確実に回避することができるので、特に高いNO_x吸着能が発現される。

【0030】Ptの担持量は、塩基性担体 120g当たり1～5gの範囲が好ましい。担持量がこれより少ないとNO_x酸化活性の低下によりNO_xの吸着能が低くなり、これより多く担持しても効果が飽和するとともにコストアップとなる。またPdの担持量は、塩基性担体 120g当たり0.5～2.5gの範囲が好ましい。担持量がこれより少ないとNO_x吸着活性の低下によりNO_xの吸着能が低くなり、これより多く担持しても効果が飽和するとともにコストアップとなる。

【0031】そして本発明の窒素酸化物吸着材は、下記のような排ガス浄化方法に用いることができる。つまり本発明の窒素酸化物吸着材を先ず酸素過剰のリーン霧囲気の排ガス中に配置して排ガス中のNO_xを吸着する。排ガス中のNO_xは、Ptの触媒作用により効率よく酸化されてNO₂となり、塩基性担体及びPdに効率よく吸着される。したがって低温域においてもNO_xをよく吸着し、吸着速度が大きく吸着量も多い。このリーン霧囲気としては特に制限がないが、空燃比(A/F)を15～50として燃焼された排ガス霧囲気が適当である。

【0032】統いて排ガス中の酸素濃度を一時的に低下させストイキーリッチ霧囲気とすると、窒素酸化物吸着材に吸着されていたNO_xが放出され、放出されたNO_xは担持されている金属ライクなPtとPdの触媒作用により排ガス中のCO、HCなどと反応して還元浄化される。このストイキーリッチ霧囲気も特に制限されないが、空燃比(A/F)を10～14程度として燃焼された排ガス霧囲気が適当である。また酸素濃度を一時的に低下させるリッチスパイクの時間あるいは頻度は、目的に応じて種々設定

することができる。

【0033】上記したように、本発明の窒素酸化物吸着材だけでも、NO_xを吸着して還元することが可能である。しかし、NO_xをさらに効率よく還元浄化するためには、本発明の窒素酸化物吸着材の下流側の排ガス流路に三元触媒又はNO_x吸収還元型触媒を配置することが望ましい。これにより窒素酸化物吸着材から放出されて窒素酸化物吸着材では還元しきれなかったNO_xを下流側の触媒で還元浄化することができ、ストイキーリッチ霧囲気におけるNO_xの排出量を一層低減することができる。また下流側の触媒にNO_x吸収還元型触媒を用いれば、上記と同様にストイキーリッチ霧囲気におけるNO_xの排出量を一層低減することができるとともに、排ガス中のNO_xが異常に多く窒素酸化物吸着材で吸着しきれなかったNO_xをNO_x吸収還元型触媒に吸収することができるので、酸素過剰のリーン霧囲気におけるNO_xの排出量も一層低減することができる。

【0034】

【実施例】以下、実施例及び比較例により本発明を具体的に説明する。

【0035】(実施例1) 水 200gに PtCl₄(5H₂O)を2.1893gと、PdCl₃(3H₂O)を2.8418gとを混合した水溶液と、水 200g 数平均分子量25,000のポリビニルピロリドン5.74gを混合した水溶液とをそれぞれ調製し、両水溶液を混合後攪拌して均一な水溶液を調製した。この水溶液に 200gのエタノールを加え、90℃で4時間環流してPt-Pd複合コロイド(Pt:50重量%、Pd:50重量%)薬液を得た。

【0036】このPt-Pd複合コロイド薬液中に所定量のZrO₂粉末を投入し、200℃で約2時間攪拌して蒸発乾固させた。これを120℃で2時間乾燥後500℃で2時間焼成し、窒素酸化物吸着材粉末を得た。この窒素酸化物吸着材粉末では、ZrO₂の120gに対してPtが1g、Pdが1g担持されている。この粉末を65MPa×2分の条件でCIP成形し、それを粉碎して大きさ0.5～0.8mmのペレット状とした。

【0037】(実施例2) 水 200gと PtCl₄(5H₂O)4.3786gとを混合した水溶液と、水 200gに数平均分子量25,000のポリビニルピロリドン5.74gを混合した水溶液とをそれぞれ調製し、両水溶液を混合後攪拌して均一な水溶液を調製した。この水溶液に100gのエタノールを加え、90℃で4時間還流してPtコロイド薬液を得た。

【0038】一方、所定量のZrO₂粉末を所定量の硝酸パラジウム水溶液の所定量中に投入し、200℃で約2時間攪拌して蒸発乾固させた。これを120℃で2時間乾燥後500℃で2時間焼成してPd/ZrO₂粉末を得た。

【0039】次に、このPd/ZrO₂粉末を上記Ptコロイド薬液中に投入し、200℃で約2時間攪拌して蒸発乾固させた。これを120℃で2時間乾燥後500℃で2時間焼成して、さらにPtを担持した。この窒素酸化物吸着材粉末

では、 ZrO_2 の120gに対してPtが1g担持され、Pdが1g担持されている。この粉末を65MPa×2分の条件でCIP成形し、それを粉碎して大きさ0.5～0.8mmのペレット状とした。

【0040】(実施例3)水200gと $PtCl_4(5H_2O)$ 4.3786gとを混合した水溶液と、水200gに数平均分子量25,000のポリビニルピロリドン5.74gを混合した水溶液とをそれぞれ調製し、両水溶液を混合後攪拌して均一な水溶液を調製した。この水溶液に100gのエタノールを加え、90℃で4時間還流してPtコロイド薬液を得た。

【0041】硝酸パラジウム水溶液中に ZrO_2 粉末を投入後、約5分後にPtコロイド薬液を投入し、200℃で約2時間攪拌して蒸発乾固させた。これを120℃で2時間乾燥後500℃で2時間焼成し、窒素酸化物吸着材粉末を得た。この窒素酸化物吸着材粉末では、 ZrO_2 の120gに対してPtが1g、Pdが1g担持されている。この粉末を65MPa×2分の条件でCIP成形し、それを粉碎して大きさ0.5～0.8mmのペレット状とした。

【0042】(比較例1)水200gと $PtCl_4(5H_2O)$ 4.3786gとを混合した水溶液と、水200gに数平均分子量25,000のポリビニルピロリドン5.74gを混合した水溶液とをそれぞれ調製し、両水溶液を混合後攪拌して均一な水溶液を調製した。この水溶液に100gのエタノールを加え、90℃で4時間還流してPtコロイド薬液を得た。

【0043】このPtコロイド薬液中に ZrO_2 粉末を投入し、200℃で約2時間攪拌して蒸発乾固させた。これを120℃で2時間乾燥後500℃で2時間焼成し、窒素酸化物吸着材粉末を得た。この窒素酸化物吸着材粉末では、 ZrO_2 の120gに対してPtが2g担持されている。この粉末を65MPa×2分の条件でCIP成形し、それを粉碎して大きさ0.5～0.8mmのペレット状とした。

【0044】(比較例2)水200gに $PtCl_4(5H_2O)$ を2.1893gと、 $RhCl_3(3H_2O)$ 2.5597gとを混合した水溶液と、水200g数平均分子量25,000のポリビニルピロリドン5.74gを混合した水溶液とをそれぞれ調製し、両水溶液を混合後攪拌して均一な水溶液を調製した。この水溶液に100gのエタノールを加え、90℃で4時間環流してPt-Rh複合コロイド(Pt:50重量%、Rh:50重量%)薬液を得た。

【0045】このPt-Rh複合コロイド薬液中に ZrO_2 粉末を投入し、200℃で約2時間攪拌して蒸発乾固させた。これを110℃で2時間乾燥後500℃で2時間焼成し、窒素酸化物吸着材粉末を得た。この窒素酸化物吸着材粉末では、 ZrO_2 の120gに対してPtが1g、Rhが1g担持されている。この粉末を65MPa×2分の条件でCIP成形し、それを粉碎して大きさ0.5～0.8mmのペレット状とした。

【0046】<試験・評価>それぞれの窒素酸化物吸着材を評価装置に配置し、図1に示す条件でNO吸着量をそれぞれ測定した。先ず N_2 ガス雰囲気にて昇温速度17.5℃

／分で室温から450℃まで加熱し、450℃で10分間保持する。その後100℃まで冷却し、表1に示すモデルガスを流して100℃で30分間NOを吸着させる。モデルガスの流量は7L／分である。その後昇温速度17.5℃／分で450℃まで加熱し、450℃で10分間保持する。そして出ガス中の NO_x 濃度を連続的に測定し、NO吸着量を求めた。それぞれの結果を図2に示す。

【0047】窒素酸化物吸着材にNOが飽和吸着すると、その後NOはPt上で NO_x ($x > 1$)となった後吸着されず素通りする。したがって、その時の入りガス(NO)と出ガス($NO + NO_x$)の差を、NO酸化活性の指標とすることができます。

【0048】

【表1】

ガス種	NO (ppm)	O_2 (%)	CO (%)	H_2O (%)	N_2
濃度	600	10	6.7	3	残部

【0049】図2より、各実施例の窒素酸化物吸着材は比較例1に比べてNO吸着量が多く、これはPtを複合コロイド薬液として担持するとともに、Ptに加えてPdをさらに担持したことに起因する効果であることが明らかである。

【0050】また実施例どうしを比較すると、実施例1より実施例2の方がNO吸着量が多く、PdをPt-Pd複合コロイド薬液を用いて担持するより硝酸パラジウム薬液を用いて担持する方が好ましいことがわかる。

【0051】また実施例3では、同じ原料を用いて得られた実施例2よりもNO吸着量が少ないが、これは実施例3ではPtとPdを同時に担持したためにPtがPdによって覆われてNO酸化活性が低下したためと考えられる。したがって先ず硝酸パラジウム薬液を用いてPdを担持し、その後Ptコロイド薬液を用いてPtを担持するのが最適であることが明らかである。

【0052】さらに比較例2のPt-Rh系の窒素酸化物吸着材では、PtとRhを共に複合コロイド薬液を用いて担持しているにも関わらず比較例1よりもNO吸着量が少なく、実施例1のPt-Pd系ほどの活性は到底得られない。これから、Rhは全く効果がなく、Pdが特異な効果を発現していることがわかり、Pdが NO_x の吸着サイトとなっていることが示唆される。

【0053】

【発明の効果】すなわち本発明の窒素酸化物吸着材によれば、低温域における NO_x 吸着量が多く、 NO_x 吸着能に優れている。したがって本発明の窒素酸化物吸着材を自動車の排ガス系に用いれば、低温域における NO_x の排出を一層抑制することができ、 NO_x 浄化率も向上する。

【図面の簡単な説明】

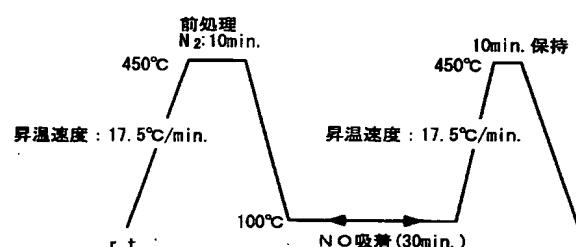
【図1】実施例における試験に用いた温度条件を示すタ

イムチャートである。

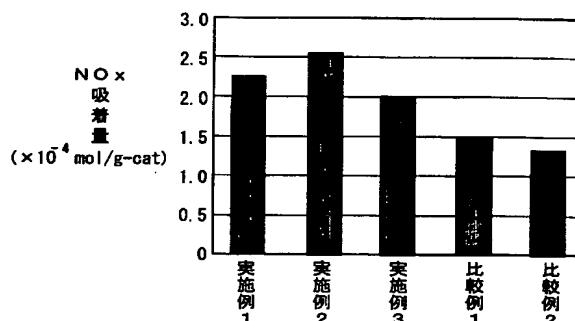
量を示すグラフである。

【図2】実施例及び比較例の窒素酸化物吸着材のNO吸着

【図1】



【図2】



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